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Infrared matrix study of reactions of propargyl halides with oxygen

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ABSTRACT

The reaction of propargyl halide with oxygen in Ar matrix has been conducted. There is no new peak was observed after the codeposition of Ar/propargyl halide. After the photolysis, a peroxide intermediate 3-(halomethyl)-1,2-dioxetene was observed first. Further photolysis led to the breakage of O-O bond of 3-(halomethyl)-1,2-dioxetene and formed final product of 3-halo-2-oxopropanal and/or 2-haloacetaldehyde and CO. The reaction mechanism was similar to that of reaction of chloroacetylene with oxygen, the additional -CH_2- group did not alter the reaction path.

KEYWORDS: IR, matrix isolation, propargyl halides, oxygen

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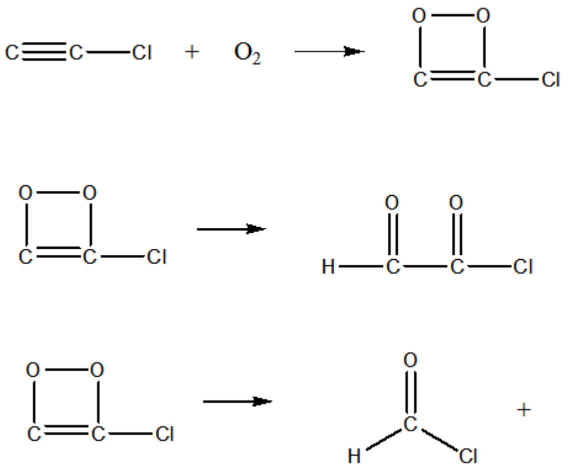
I. INTRODUCTION

Propargyl halide has similar character as allyl halide which has both halide atom and unsaturated bond. These characteristics let allyl halides can undergo alkyl halide reaction and unsaturated alkene reaction and became an important chemical intermediates. Although propargyl halide and allyl halide have similar character, both halide atom and unsaturated bond, which can undergo alkyl halide reaction and unsaturated alkene reaction. These characteristics let allyl halides became an important chemical intermediates. Although the addition reaction of propargyl halide is not easy as allyl halide, alkyne has twoπ-electrons led to more type of reactions. Therefore, the relative reaction of ozone with alkenes and alkynes gave a lot interesting in atmosphere chemistry.[1-6]

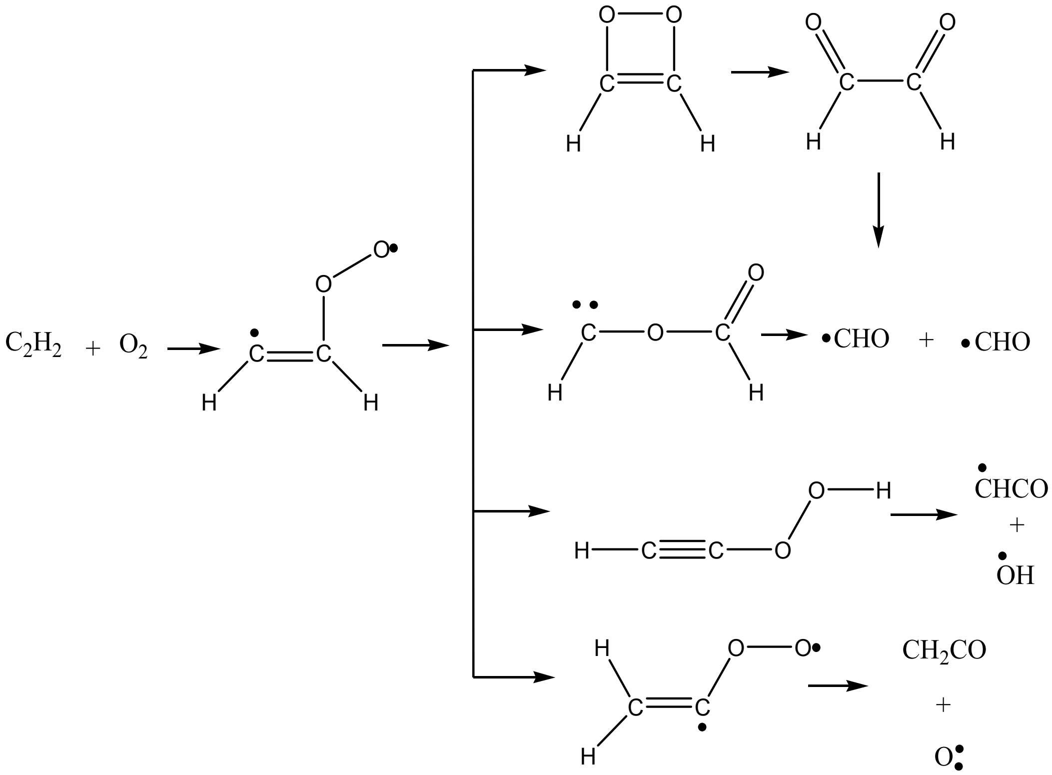
Most reaction of alkynes with oxygen molecule are based on theoretical calculation to study its reaction mechanism.[6] In previous study[7], the reaction of acetylene chloride with O_2 in Ar matrix has been studied by FTIR/matrix isolation technique and proposed possible mechanism as scheme I. Oxygen was added to the triple bond and formed a peroxide intermediate HC(OO)CCl which was then undergo O-O breakage and decomposed to final products of HC(O)C(O)Cl or HC(O)Cl with CO molecule.

Scheme I[7]



Laskin et. al[8] have applied calculation software and kinetic model to study analyze the initial mechanism of oxidation of acetylene in shock tube, and proposed the mechanism as scheme II.

Scheme II[8]



Until now, there is only very few data about the reaction of propargyl halide with oxygen and no related study for the isolation and identification of intermediate and products. Literature study of Chloroacetylene has an electron withdrawing -Cl group connected to CC triple bond, while propargyl halide has-CHCl group connected to triple bond, whether the $–CH_2$-group will affect the breakage of O-O bond. Matrix isolation technique [9-11] was developed in mid-1950's and applied to the study of unstable molecules and free radicals.[12] Therefore, this research will applied matrix isolation/infrared spectrum to study the photolysis of propargyl halides/oxygen in Ar matrix, the isolation and identification of intermediate and product was useful for understanding the reaction mechanism.

II. EXPERIMENTAL

All of the experiments were carried out on conventional matrix isolation setup as previous.[13,14]The experimental system consisted of four basic parts, the cryogenic system, the cold cell vacuum vessel, the vacuum system, and Fourier transform infrared spectrometer. Cryogenics were supplied by a CTI M-22 cold head unit and a CTI 8200 helium closed cycle refrigerator, which maintained a temperature below 12 K. The temperature at the cryogenic CsI surface was monitored by a silicon diode thermal sensor (Lake Shore Model 321 auto temperature controller). The window temperature was regulated by supplying a constant voltage to a 25 W cartridge heater mounted on the cold copper block to anneal tile matrix or warm the matrix at the end of experiment. The vacuum vessel was equipped with CsI windows and quartz windows and sat in tile sample beam of the infrared spectrometer. The vacuum manifold was stainless steel (Cajon fitting) with Nupro valves.

The samples of Ar (99.9995%, Lien Hwa) and O_2 (99.995%, San Fu or Matheson) were used as received. Propargyl bromide C_3H_3Br (99%, Aldrich) and propargyl chloride C_3H_3Cl (98%, ACROS) were purified by trap-to-trap distillation before use. The concentration of matrix/reactant (M/R) ratio was in the range of 200/1 to 2000/1. Sample was deposited via single jet mode with rate of ~ 2 mmol/h for about 1.5 hours before spectra were recorded. Infrared spectra were recorded on a Perkin Elmer Model 2000 FTIR spectrometer with MCT detector at a resolution of 2 cm^{-1} with 64 scans average. The photolysis was applied with a 200 W Hg lamp by in-situ photolysis or photolysis during deposition.

III. RESULTS

The deposition and IR spectrum measurement of blank parent reagent were conducted. In each case, the blank spectra were in good agreement with literature spectra.[15]

Ar/Propargyl Chloride (C_3H_3Cl) The deposition of Ar/C_3H_3Cl at varied concentration (2000/1~200/1) were conducted and infrared spectrum were measured. There is one new peak at 867 $cm^{-1}$was observed and increased in intensity as concentration of C_3H_3Cl increased. The infrared spectrum before and after photolysis were shown in Figure 1 and the positions of absorption were summarized as Table 1.

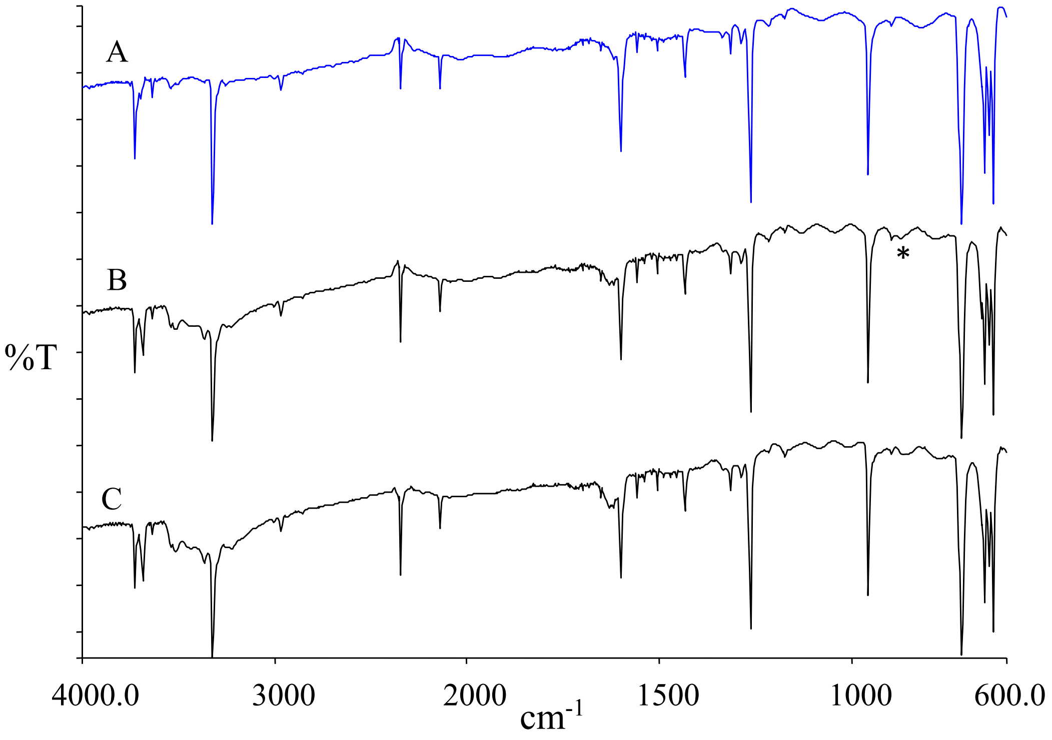


Fig. 1 Infrared spectra of Ar/C_3H_3Cl before and after photolysis at various time. (A) 0 min； (B) 60 min；(C) 90 min

Table 1 The frequency positions (cm^{-1}) of IR spectrum of Ar/propargyl chloride (2000/1)

Ar matrix	Literature (gas)[15]	assignment
3328,3324	3342,3335,3326	ν_1(CH)
	3002	$\nu_{11}(CH_2)$
2973,2963	2975,2961	$\nu_2(CH_2)$
2855(vw)	2872,2855	$\nu_3+\nu_7$
	2700	$\nu_4+\nu_5$
	2520	$2\nu_5$
2339, 2345	2339	$\nu_4+\nu_{13}$
2142	2151,2147,2138	ν_3, C≡C
1436	1450,1433	ν_4, CH_2 bend

1317	1330,1318,1308	$2\nu_8$
	1298,1288	$2\nu_{14}$, $\nu_8+\nu_{14}$
1269,1263	1277,1271,1262	ν_5, CH_2 wag
1216,1211	1220,1213,1206	$\nu_{13}+\nu_{15}$
1174	1179	ν_{12},CH_2, twist
960	968,960,952	ν_6,C-C
899	903,898,890	$\nu_{10}+\nu_7$
852	840,827	$\nu_{10}+\nu_8$
730,726, 719,715	732,725,718	ν_7, C-Cl
659	651,645	ν_8,CH bend
635	637	ν_{14}, CH bend

*：The low frequency below 600 cm^{-1} were not list here.

Ar/Propargyl Bromide (C_3H_3Br) The spectrum was taken after the deposition of Ar/C_3H_5Br (2000/1), the absorption positions were similar to literature spectrum in gas phase. The spectrum was shown in Figure 2 and position of absorption peak were listed on Table 2. After the photolysis, several new peaks were detected at 3068、1965、1425、1212、1199、1082、996、865、804、and 675 cm^{-1} and summarized at Table 3.The new bands at 865、804、and 675 cm^{-1} were not belong to the absorption of propargyl chloride. These new bands were enhanced as the time of photolysis increased. The peak at 865 cm^{-1} is belong to the vibration of CH_2 rocking, 804 cm^{-1} is due to the CH_2 bending vibration, and 675 cm^{-1} is C-Br stretching vibration mode. The absorption positions of these new band were similar with the vibrational modes of bromopropadiene. The intensities of these new peak were increased as the concentration of Ar/C_3H_5Br was increased to 500/1 and 200/1.

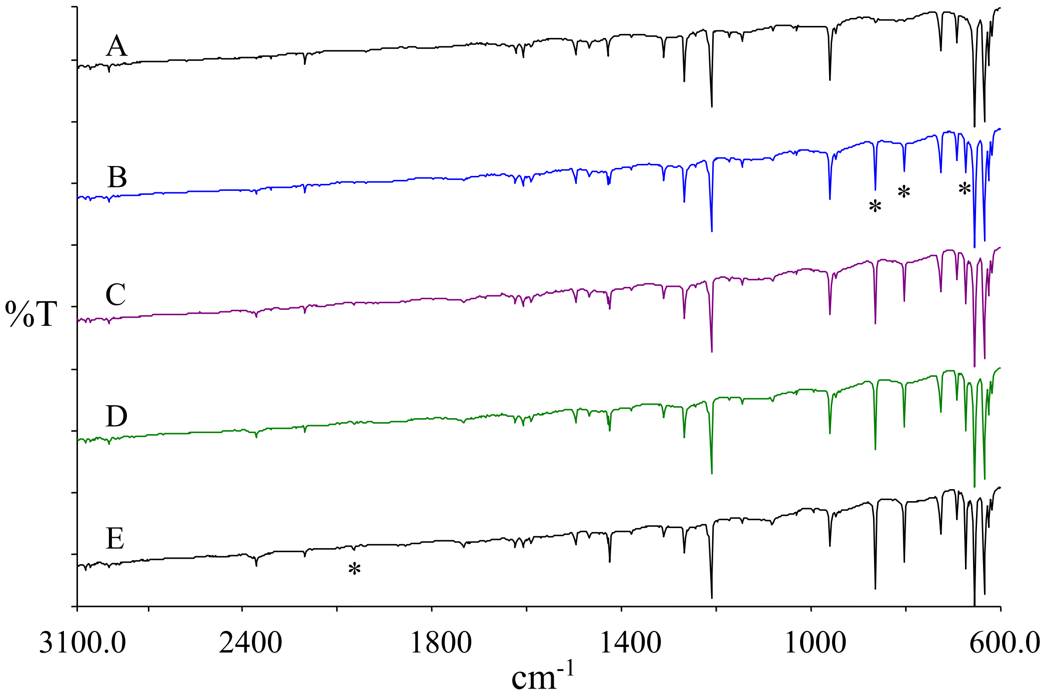


Fig. 2 Infrared spectra of Ar/propargyl bromide (2000/1) before and after photolysis in the range at 3100-600 cm^{-1}. (A) 0 min； (B) 10 min； (C) 30 min； (D) 60 min； (E) 90 min

Table 2 The frequency positions (cm^{-1}) of IR spectrum of propargyl bromide (2000/1) in Ar matrix at 10K

Ar /C_3H_3Br (2000/1)	Literature (gas)[15]	Assignment
3329	3341,3335,3328	ν_1, CH asym. st.
3316	3310	$\nu_1+\nu_8-\nu_8$
	3008*	ν_{11} CH_2
2970	2982,2970	ν_2, CH_2 asym. st.
2844	2856,2840	$2\nu_4$
2639	2652,2638	$\nu_4+\nu_5$
2414	2428,2414	$2\nu_5$
	2290	$\nu_4+\nu_{13}$
2173	2180,2168	$\nu_5+\nu_6$
2137	2145,2130	ν_3
1497,1468,1430	1440,1431,1427	ν_4, CH_2 bend
1311	1322,1314	$2\nu_8$
1268	1279,1268	$2\nu_{14}$, $\nu_8+\nu_{14}$
1212	1223,1218,1212	ν_5, CH_2 wag
1173	1177,1169,1164	$\nu_{13}+\nu_{15}$
1146	1152	ν_{12}, CH_2 twist
1038	1040	impurity
961	968,961,954	ν_6
865	866*	ν_{13}, CH_2 rock
804	810	impurity
656	650	ν_8, CH bend
626、637	637	ν_{14}, CH bend
619	618	ν_7,C-Br st.

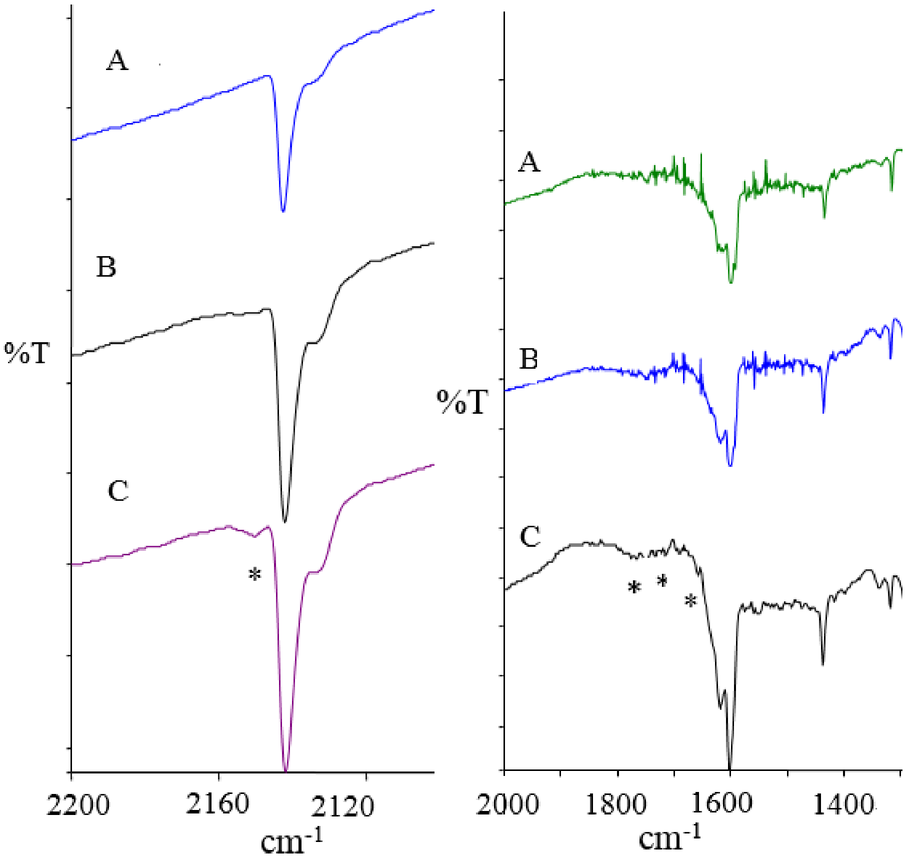
*: solution phase

Table 3. The positions of new peaks (cm^{-1}) of Ar/propargyl bromide after photolysis.

Ar matrix	Literature(gas)[13] $H_2C=C=C-Br$	assignment
	3086,3073(m)	ν_{11}, CH_2 asym. st.
3068		ν_1, CH_2 asym. st.
	3005(m)	ν_{12}, CH_2 asym. st.
1965.93	1961(w)	ν_3, C=C=C asym. st.
1425.48	1432(s)	ν_4, CH_2 bend, a’
1212.2	1223,1211(vs)	ν_5, CH bend

1199(vw)	1181,1172	$\nu_{12}+\nu_{15}$
1082.39	1078	ν_6,C=C=C sym. st.
996.63	1000	ν_{12}, CH_2 rock
865.65	862	ν_7, CH_2 wag.
804.94	812	ν_{13}, CHbend
675.09	681	ν_8, CBr st.
	603	ν_9,C=C=C bend, a'

Ar/C_3H_3Cl/O_2 The spectra were not apparent changed before and after in-situ photolysis with Hg lamp. The photolysis during deposition was conducted, the intensity of parent bands of propargyl chloride were decreased after 60 min photolysis and new bands at 1656, 928, 875, and 718 cm^{-1} were observed. As the photolysis last 90 minutes, further new bands at 1758, 1737, 1054, and 760 cm^{-1} were observed. The intensity of 718 cm^{-1} was enhanced. The spectral change before and after photolysis and the position of new peaks were summarized as Figure 3 and Table 4, respectively.



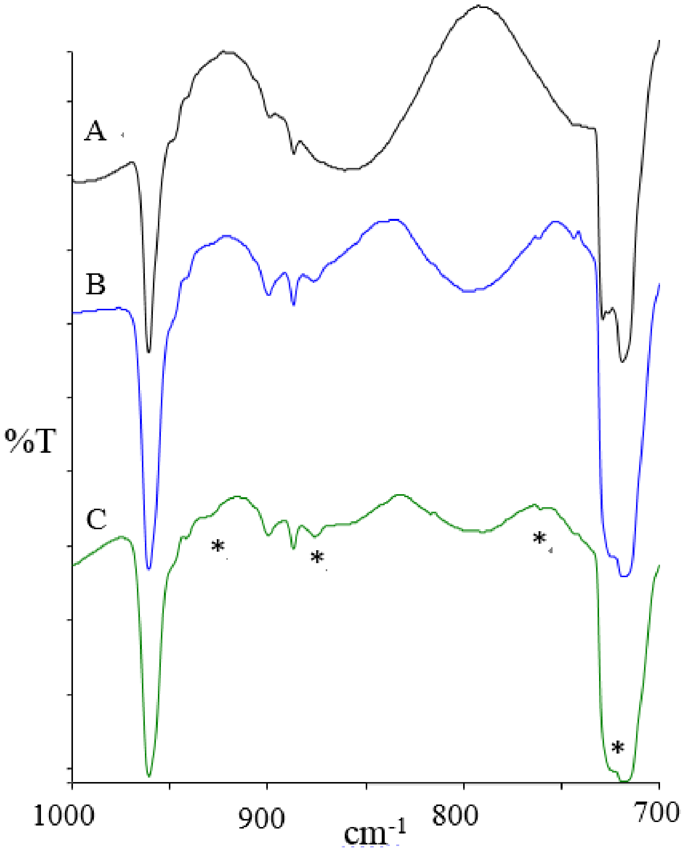


Fig. 3 Infrared spectra of Ar/propargyl chloride before and after photolysis during deposition. (A) 0 min; (B) 60 min; (C) 90 min

Table 4. The peak position of new absorption (cm^{-1}) of Ar/C_3H_3Cl/O_2 matrix after photolysis at various time.

Photolysis time (min)	exp't frequency (cm^{-1})	calculation frequency^{*,16}	assignment
60	1656	1658	C=C st.
	928	939	asym C-O st.
	875	852	skeletal ring bend
	718	700	C-Cl st.
90	1748	1752	asymC=O st.
	1737	1737	C=O st.
	760	762	C-Cl st.
	718	715	C-Cl st.

*：Calculation frequencies of 3-(chloromethyl)-1,2-dioxetene、3-chloro-2-oxopropanal、and 2-chlloroacetaldehyde, unpublished results.

Ar/C_3H_3Br/O_2 The in-situ photolysis after deposition of Ar/C_3H_3Br (2000/1~100/1) with O_2 gave no spectral change, while the photolysis during deposition about 60 min led to the decrease in intensity of parent bands of propargyl bromide and the observation of several new absorption peaks at 1669, 930, 673, and 618 cm^{-1}. Further photolysis gave additional new bands at 1770, 1733, 1022, and 1004 cm^{-1} and the enhancement in intensity of 618 cm^{-1}. The original new peaks after photolysis Ar/C_3H_3Br at 865, 804, and 675 cm^{-1} were increased in intensities and the bands at 1965 and 1982 cm^{-1} became very weak. The spectral change before and after photolysis at various time were shown as Figure 4and Figure 5. The positions of observed new bands are summarized as Table 5.

Table 5. The peak position of new absorption (cm^{-1}) of Ar/C_3H_3Br/O_2 matrix after photolysis at various time.

photolysis time (min)	**exp't frequency (cm^{-1})**	**calculation frequency$^{*,[16]}$**	**assignment**
60	1669	1652	C=C st.
	930	930	asym C-O st.
	673	673	C-H bend

	618	619	C-Br st.
90	1770	1752	asym C=O st.
	1733	1730	C=O st.
	1022	1022	C-C st.
	1004	1004	C-C st.
	618	598	C-Br st.

*: Calculation frequencies of 3-(bromobrmethyl)-1,2-dioxetene, 3-bromo-2-oxopropanal, and 2-bromoacetaldehyde,unpublished results.

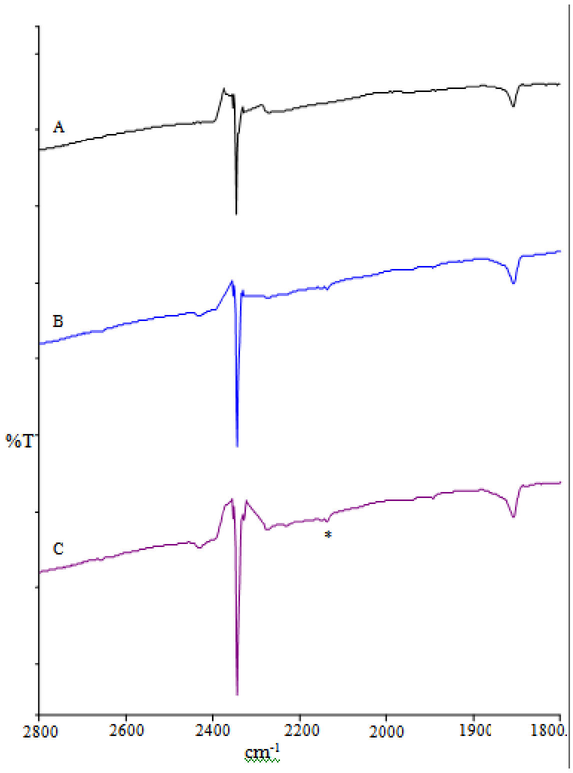


Fig. 4 Infrared spectra of Ar/propargyl bromide before and after photolysis during deposition (2800-1800 cm^{-1}). (A) 0 min; (B) 60 min; (C) 90 min

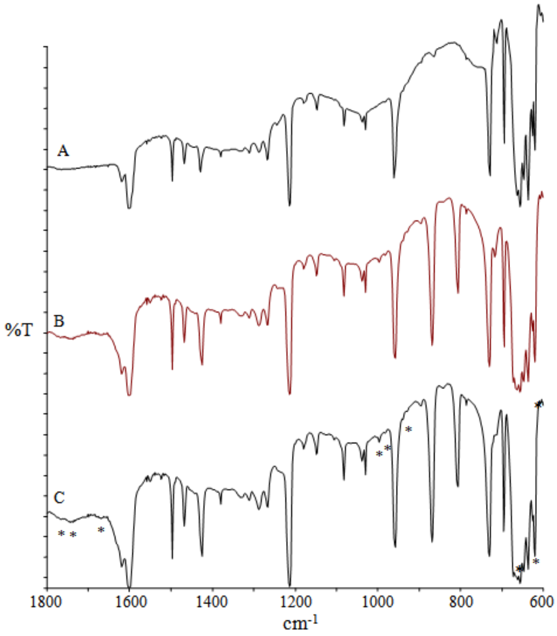


Fig. 5 Infrared spectra of Ar/propargyl bromide before and after photolysis during deposition (1800-600 cm^{-1}). (A) 0 min; (B) 60 min; (C) 90 min

Band Assignment

Previous study of alkenyl chloride/O_2 indicated that O_2 would add to the unsaturated C=C bond and formed peroxide product 3-(halomethyl)-1,2-dioxetane. Also, referred to the study of reaction of acetylene/O_2 and acetylene chloride/O_2 which gave the product of 2-chloro-1,2-dioxetene and HC(O)C(O)Cl. If the reaction of propargyl halide with O_2 is similar to the reaction of acetylene chloride/O_2, the possible product will be 3-(halomethyl)-1,2-dioxetene and $HC(O)C(O)CH_2X$. Therefore, the band assignment will accomplished by comparison of observed vibrational bands to the literature value and theoretical calculated frequency of 3-(halomethyl)-1,2-dioxetene and $HC(O)C(O)CH_2X$.

Ar/C_3H_3Cl/O_2 The new bands observed after the photolysis of Ar/C_3H_3Cl/O_2 were 1656, 928, 875, and 717 cm^{-1}. The stretching vibrational mode of C=C bond is in the range of 1690~1635 cm^{-1}, the calculated value of C=C stretching mode of 3-(chloromethyl)-1,2-dioxetene is 1658 cm-1, therefore 1656 cm^{-1} can be easily assigned as C=C stretching mode. Another new peak of 928 cm^{-1} can be assigned as the C-O stretching mode of 3-(chloromethyl)-1,2-dioxetene which is 939 cm^{-1} by calculation. The third new band of 875 cm^{-1} is closed to the cycling skeletal bending mode of, 3-(chloromethyl)-1,2-dioxetene, therefore this band can be assigned as the skeletal bending mode. The intensity of parent band 718 cm^{-1} was increased after photolysis. The theoretical value of C-Cl stretching of molecule 3-(chloromethyl)-1,2-dioxetene is 700 cm^{-1}, the band of 717 cm^{-1} can be assigned as C-Cl stretching mode. Based on the character of these new band, above new band should belong to the vibrational modes of 3-(chloromethyl)-1,2-dioxetene.

After the photolysis of 90 min, two new bands were observed at 1748 cm^{-1} and 1737 cm^{-1}, which is in the range of C=O stretching mode. The breakage of O-O bond of 3-(chloromethyl)-1,2-dioxetene will form 3-chloro-2-oxopropanal ($HC(O)C(O)CH_2Cl$) or 2-chloroaldehyde ($HC(O)CH_2Cl$) with CO. The calculated value of asymmetry and symmetry C=O stretching mode of $HC(O)CH_2Cl$ is 1752 cm^{-1} and 1737 cm^{-1}, respectively. Therefore, 1748 cm^{-1} and 1737 cm^{-1} cab be assigned as asymmetry C=O mode of $HC(O)C(O)CH_2Cl$ and symmetry C=O stretching mode of $HC(O)CH_2Cl$. The band at 717 cm^{-1} is closed to the calculated frequency of C-Cl stretching vibrational mode of $HC(O)C(O)CH_2Cl$ (715 cm^{-1}) which resulted in the enhancement in intensity of parent band of 718 cm^{-1}. The another weak band at 760 cm^{-1} is agreed with the calculated value 762 cm^{-1} of C-Cl of $HC(O)CH_2Cl$. Therefore, the peaks of 760 and 717ncm^{-1} can be assigned as the C-Cl stretching mode of $HC(O)CH_2Cl$ and $HC(O)C(O)CH_2Cl$ molecule, respectively. The new absorption at 2149 cm^{-1} is belonged to the absorption of CO molecule. All the above suggested that the second group of new peaks are due to the product formation of $HC(O)C(O)CH_2Cl$ or $HC(O)CH_2Cl$ with CO

Ar/C_3H_3Br/O_2 The photolysis of Ar/C_3H_3Br led to many new absorptions which are consisted with literature data[32] of vibrational frequencies of 1-bromo-1, 2-butadiene as listed in Table 3. Therefore, these new bands can be assigned as the vibrational modes of 1-bromo-1, 2-butadiene.

Similar to the results of Ar/C_3H_3Cl/O_2 and comparison with the frequencies of 3-(bromomethyl)-1,2-dioxetene, $HC(O)C(O)CH_2Br$ or $HC(O)CH_2Br$. The peak at 2138 cm^{-1} can be assigned as the vibrational absorption of CO molecules. The peak at 1669 cm^{-1} and 930 cm^{-1} was the C=C stretching mode and asymmetry C-O stretching mode of 3-(bromomethyl)-1,2-dioxetene, which is 1652 cm^{-1} and 930 cm^{-1} of calculated frequency, respectively. The peak of 673 cm^{-1} is same as the calculated frequency of C-H bending mode of 3-(bromomethyl)-1,2-dioxetene. The parent band at 618 cm^{-1} was increased in intensity and broaden, this might due to the C-Br stretching mode of 3-(bromomethyl)-1,2-dioxetene with a calculated value of 619 cm^{-1}. From the above the new absorption of first group after photolysis is due to the product of 3-(bromomethyl)-1,2-dioxetene.

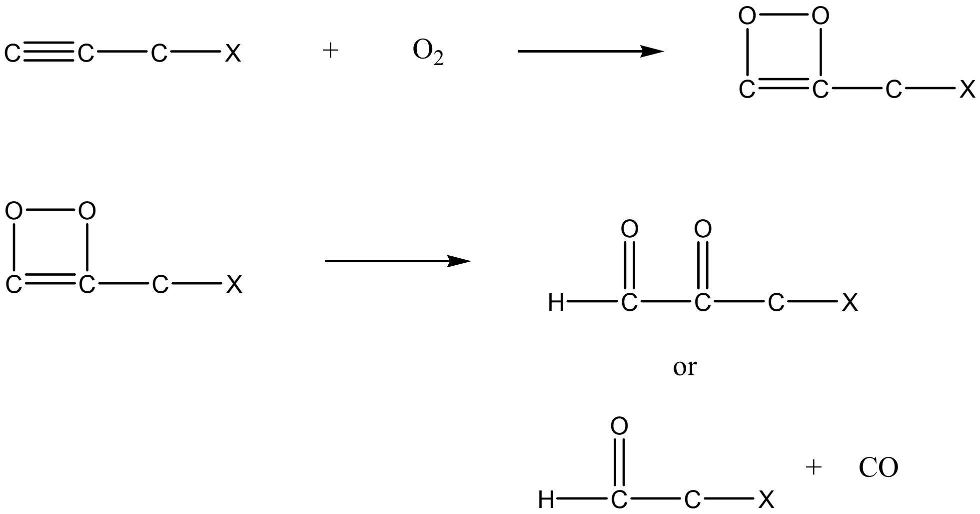
After 90 min photolysis, the positions of new group were similar to that of product of Ar/C_3H_3Cl/O_2 reaction, therefore, the assignment of new peaks were directly. 1770 cm^{-1}, 1733 cm^{-1}, 1022 cm^{-1} and 1004 cm^{-1} can be assigned as the asymmetry stretching of 3-bromo-2-oxopropanal ($HC(O)C(O)CH_2Br$), symmetry C=O stretching of 2-bromoaldehyde ($HC(O)CH_2Br$), C-C stretching mode of $HC(O)C(O)CH_2Br$, and C-C stretching mode of $HC(O)CH_2Br$, respectively. Similarly, the broaden and enhancement of 618 cm-1 due to the C-Br stretching of $HC(O)CH_2Br$ and $HC(O)C(O)CH_2Br$, which is 598 cm-1 and 638 cm-1 from the calculation. All the above indicated the new absorption of second group were arisen from the product of $HC(O)C(O)CH_2Br$, $HC(O)CH_2Br$ and CO.

IV. DISCUSSION

Based on the comparison of new absorption peaks with literature and calculation frequencies confirmed the first observation of intermediate of 3-(halomethyl)-1,2-dioxetene, further photolysis will led to the formation of final product of 3-halo-2-oxopropanal, 2-haloacetaldehyde and CO. The structure of these products were similar to that of HCCCl/O_2 reaction. The photolysis of oxygen might produce ozone which might further reacted with propargyl halide to form new product. However, we did not detected another further new absorption peak in spectrum. The photolysis of propargyl bromide resulted in the formation of allenyl bromide which might also reaction with oxygen, again, there is no new band was observed. All the above suggested the reaction of propargyl halide/O_2 is similar to the reaction of chloroacetylene/O_2, the possible mechanism was proposed as Scheme III.

The oxygen was added to C ≡ C triple bond and formed peroxide intermediate, 3-(halomethyl)-1,2-dioxetene, further photolysis led to the breakage of O-O bond and formed product of 3-halo-2-oxopropanal or 2-haloacetaldehyde and CO. The reaction mechanism was similar to the reaction of chloroacetylene with oxygen, the -CH_2- group did not alter the reaction path.

Scheme III



V. CONCLUSION

The reaction of propargyl halide with oxygen in Ar matrix has been conducted. Based on the observation of new IR peaks after photolysis and comparison with literature and calculated frequencies, a peroxide intermediate, 3-(halomethyl)-1,2-dioxetene was formed first. Further photolysis led to the breakage of O-O bond of 3-(halomethyl)-1,2-dioxetene and formed final product of 3-halo-2-oxopropanal and/or 2-haloacetaldehyde and CO. The reaction mechanism was similar to that of reaction of chloroacetylene with oxygen, the additional -CH_2- group did not alter the reaction path.

REFERENCES

[1]. R. Criegee, *Angew. Chem. Int. Ed.*, 1975, 14, 745-752.
[2]. C. K. Kohlmiller and L.Andrews,*J. Am. Chem. Soc.*, 1981, 103, 2578-2583.
[3]. R. J. H. Clark and L. J. Foley, *J. Phys. Chem. A*, 2002, 106, 3356-3364.
[4]. U. Samuni, R. Fraenkel, Y. Haas, R. Fajgar, and J. Pola,*J. Am. Chem. Soc.*, 1996, 118, 3687-3693.
[5]. R. Criegee, M. Lederer, M. Liebigs, *Ann. Chem.*, 1953, 583, 29.
[6]. D. Cremer, R. Crehuet, and J. Anglada,*J. Am. Chem. Soc.*, 2001, 123, 6127-6141.
[7]. M.-L. Hwang, W.-L. Hsu,*J. Mol. Struct.*, 1998, 449, 29-37.
[8]. A. Laskin, H. Wang, *Chem. Phys. Lett.*, 1999, 303, 43–49.
[9]. E. Whittle, D.A. Dows, G.C. Pimentel, *J. Chem. Phys.*, 1954, 22,1943.
[10]. S. Graddock, A. Hinchliff, ”Matrix Isolation”, Cambridge University Press : New York, **1975.**
[11]. L. Andrew, *Annu, Rev. Phys. Chem.*, 1971, 22, 109.
[12]. B.S. Ault, *Rev. Chem. Intermed.*, 1988, 9, 233.
[13]. Y.-W. Wu, M.-L. Hwang, W.-L. Hsu and F.-H. Fang, *J. Chin. Chem. Soc.*, 1998, 45, 307-312.
[14]. R. Jeng, J.-F. Yang, M.-S. Wu, M.-L. Hwang, *The International Journal of Engineering and Science*, 2020, 9(2), 61-64.
[15]. J. C. Evans and R. A. Nyauist, *Spectrochimica. Acta*, 1963, 19, 1153-1163.
[16]. M. L. Hwang, C. L. Pan, calculation with Gaussion 03software,unpublished result.

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